Support modification to improve the sulphur tolerance of Ag/Al$_2$O$_3$ for SCR of NO$_x$ with propene under lean-burn conditions

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ABSTRACT

Ag/Al$_2$O$_3$ catalysts with 1 wt% SiO$_2$ or TiO$_2$ doping in alumina support have been prepared by wet impregnation method and tested for sulphur tolerance during the selective catalytic reduction (SCR) of NO$_x$ using propene under lean conditions. Ag/Al$_2$O$_3$ showed 44% NO$_x$ conversion at 623 K, which was drastically reduced to 21% when exposed to 20 ppm SO$_2$. When Al$_2$O$_3$ support in Ag/Al$_2$O$_3$ was doped with 1 wt% SiO$_2$ or TiO$_2$ the NO$_x$ conversion remained constant in presence of SO$_2$ showing the improved sulphur tolerance of these catalysts. Subsequent water addition does not induce significant deactivation. On the contrary, a slight promotional effect on the activity of NO conversion to nitrogen is observed after Si and Ti incorporation. FTIR study showed the sulphation of silver and aluminum sites of Ag/Al$_2$O$_3$ catalysts resulting in the decrease in the formation of reactive intermediate species such as –NCO, which in turn decreases NO$_x$ conversion to N$_2$. In the case of Ag/Al$_2$O$_3$ doped with SiO$_2$ or TiO$_2$, formation of silver sulphate and aluminum sulphate was drastically reduced, which was evident in FTIR resulting in remarkable improvement in the sulphur tolerance of Ag/Al$_2$O$_3$ catalyst. These catalysts before and after the reaction have been characterized with various techniques (XRD, BET surface area, transmittance FTIR and pyridine adsorption) for physico-chemical properties.

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1. Introduction

Removal of NO$_x$ from the exhaust gases of lean-burn and diesel engines is a major challenge to fulfil future restrictive standard emissions. Hydrocarbon selective catalytic reduction (HC–SCR) of NO$_x$ is a powerful technology for the removal of nitrogen oxides, carbon monoxide and unburned hydrocarbon from automotive emissions except under a large excess of oxygen. In such conditions, a narrow operating window is usually reported for the conversion of NO$_x$ accompanied with a significant production of nitrous oxide [1]. Numerous studies dealt with this topic over a wide variety of catalytic systems such as metal oxides [2], zeolites [3,4] and noble metal supported aluminas [5], which have been found to be active for this reaction depending on the running temperature. Out of these, Ag/Al$_2$O$_3$ is one of the most active and selective for the SCR of NO$_x$ to N$_2$. The main advantage of this system is its inherent thermal and hydrothermal stability [6], and its wide operating window observed for the selective conversion of NO to nitrogen particularly in presence of heavy hydrocarbons and hydrogen [7].

The lean-burn engine exhausts typically contain water and SO$_2$. The presence of water is usually known to cause deactivation of the catalyst. However this deactivation is known to be reversible upon removal of water from the feed. Deactivation of the catalyst due to SO$_2$ in the exhaust gases is one of the major limitations of this catalyst system for its practical applications and has been correlated to the formation of sulphate species on the catalyst surface. Therefore it becomes essential that the catalysts should be stable and active in the presence of water vapor and SO$_2$. Most researchers have demonstrated the effect of SO$_2$ [8–10] and SO$_2$ + H$_2$O [11,12] on Ag/Al$_2$O$_3$ system. Meunier and Ross [8] reported the effects of SO$_2$ on the lean deNO$_x$ activity of 1.2 wt% Ag/Al$_2$O$_3$ with C$_3$H$_6$. The sample was rapidly and permanently deactivated after exposure to 100 ppm SO$_2$ at 759 K, which was attributed to the formation of surface silver sulphate species. Jen [9] also found that the NO$_x$ conversion dropped over 2 wt% Ag/Al$_2$O$_3$ catalysts from 62% to 28% when the catalyst was tested with a mixture of propene and propane in presence of 18 ppm SO$_2$. In contrast, Park et al. [10] who studied the effect of SO$_2$ on the activity of Ag/Al$_2$O$_3$ with various Ag loadings on a C$_3$H$_6$–SCR for NO concluded that the improvement in the NO$_x$ conversion was due to the formation of Ag$_2$SO$_4$ phase. These authors observed correlatively an enhancement of –NCO species formation and the suppression of propene oxidation compared to Ag$_2$O. The decrease of catalytic performance in presence of SO$_2$ was mainly due to the poisoning of

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alumina active sites, which are also responsible for NO reduction to N_2. It was concluded that the addition of SO_2 enhanced the performance of silver sites, but hindered the NO reduction function of alumina sites. In another study, Abe et al. [11] reported excellent NO_x reduction and SO_2 tolerance with ethanol as the reductant above 700 K in presence of 10% O_2, 10% H_2O, and 30–80 ppm SO_2 on Ag/Al_2O_3 with higher silver loading (4.6%). The authors suggested that silver sulphate should be catalytically active for NO_x reduction at temperatures above 700 K. Sumiya et al. [12] have also reported high NO_x conversion (80%) with ethanol for a 4 wt% Ag/Al_2O_3 even after 10% H_2O and 30 ppm SO_2 were introduced. Angelidis et al. [13] have reported a promotional effect on the catalytic reduction of NO_x over 5 wt% Ag/Al_2O_3 upon addition of 25–100 ppm SO_2 at 753 K in presence of excess oxygen and a mixture of propane/propene. The promotional effect was clear over long-term experiments up to 15 h and the catalyst activity was stabilized earlier in presence of SO_2. The authors attributed the promotional effect to the formation of hydrocarbon oxygenates, sulphur accumulation on the catalyst surface and change in the deNO$_x$ reaction mechanism. The additive effect of noble metals for NO reduction by hydrocarbons has also been reported in the literature [14,15]. Lee et al. [14] found that addition of Pd improved the water tolerance of Co-FER system in the SCR of NO_x by CH_4. The improved water tolerance was attributed to the role of Pd in the oxidation of NO to NO_2, an intermediate in the NO reduction and enhanced NO adsorption on the catalyst surface. In another study, the addition of 0.01 wt% Pd into a 5 wt% Ag/Al_2O_3 system increased the reaction activity of NO at low temperatures. However the catalytic activity drastically decreased in presence of SO_2 due to Ag_2SO_4 phase, the formation of which was enhanced by Pd [15]. *In situ* DRIFTS results suggested that Pd addition catalyzed the partial oxidation of C_3H_6 into a surface enolic species, which are reactive towards NO_3^- to form a surface –NCO species. In presence of SO_2, the formation of these intermediate species was inhibited, hence the decrease in activity [15]. Incorporation of SiO_2 in this system increased the sulphur tolerance of the Ag–Pd/Al_2O_3 system. Addition of SiO_2 enhanced the formation of the intermediate species (NO_3^-, enolic and –NCO species) and hence the high activity in the NO_x reduction when the gas feed contained SO_2 [16].

From the above discussion it is clear that the main reason for the deactivation of SCR catalysts is the sulphation of the active metal (Ag, Pd, etc.) and the support (Al_2O_3). One way of improving the sulphur durability of alumina based SCR catalyst is by modification of the support so as to make it more sulphur tolerant. One strategy is to facilitate the decomposition of sulphates by adding certain materials to the catalyst like SiO_2 or TiO_2. SiO_2 and TiO_2 were chosen as the additives because these are weakly sulphating supports and it is well known that the sulphates of SiO_2 and TiO_2 decompose at lower temperatures than those of Al_2O_3 [17,18]. With the aim of improving the sulphur tolerance of the Ag/Al_2O_3 based system, in the present work, 2 wt% Ag/Al_2O_3 catalyst was prepared by wet impregnation method and the Al_2O_3 support was modified by incorporation of SiO_2 or TiO_2. The influence of these additives on the nature of adsorbates by *in situ* spectroscopic measurements (using DRIFT) with further comparison of catalytic performances in terms of NO conversion to nitrogen was carefully examined in order to investigate the possible intermediates or strongly adsorbed species which may cause inhibiting effects.

2. Experimental

2.1. Catalyst preparation

Alumina-supported silver catalyst (2 wt% Ag, labeled as AgAl) was prepared by impregnation of commercially available boehmite (AlOOH) with aqueous silver nitrate solution. The sample was dried overnight at 373 K and calcined in air at 773 K for 6 h. For the preparation of 1 wt% SiO_2 incorporated AgAl, 0.347 g Si[OC_2H_5]$_4$ was dissolved in isopropyl alcohol. This solution was added to boehmite (14.3 g) dispersed in isopropyl alcohol under constant stirring. The solution was evaporated and the sample dried overnight at 373 K. To this dried sample aqueous silver nitrate solution (0.315 g) was added, stirred on a hot plate and dried overnight at 373 K and subsequently calcined in air at 773 K for 6 h. The above procedure was repeated for the preparation of TiO_2 incorporated Al_2O_3 sample with Ti[OC_4H_9]$_4$ (0.439 g) as the titanium source followed by Ag impregnation. The material was dried at 373 K and subsequently calcined at 773 K for 6 h. The final samples were labeled as AgSiAl and AgTiAl respectively. In order to study the effect of amount of additive on the SCR of NO_x, additional two samples with 2 wt% of SiO_2 and TiO_2 were prepared by the method discussed above and were labeled as Ag2SiAl and Ag2TiAl respectively.

2.2. Catalyst characterization

2.2.1. Powder X-ray diffraction studies

The powder X-ray diffraction data of the samples was collected on a Rigaku Miniflex diffractometer equipped with a Ni filtered Cu Kα radiation (λ = 1.5406 Å, 30 kV, 15 mA) radiation. The data was collected in the 2θ range 20–80° with a step size of 0.02° and scan rate of 4° min^{-1}.

2.2.2. Nitrogen adsorption studies

The BET surface area of the calcined samples was determined by N_2 sorption at 77 K using NOVA 1200 (Quanta Chrome) equipment. Prior to N_2 adsorption, the materials were evacuated at 573 K under vacuum. The specific surface area, S_{BET}, was determined according to the BET equation.

EDAX-analysis: EDAX analysis was carried out using Quanta 200 3D with EDAX at 30 kV.

2.2.3. FT-IR of adsorbed pyridine

The nature of the surface acid sites was studied by FTIR of adsorbed pyridine at room temperature. The FT-IR spectra of chemisorbed pyridine (Py-IR) were obtained in a high temperature cell (Spectra-Tech) fitted with a ZnSe window (Shimadzu 8000 FTIR spectrophotometer). The temperature in the cell was varied from 303 K to 698 K. The sample (30 mg) was finely crushed and placed in a sample holder. Prior to pyridine adsorption, the sample was out gassed for 2 h at 698 K under N_2 flow to remove adsorbed moisture. The cell was cooled to room temperature stepwise and the spectra of neat catalyst were recorded (250 scans resolution 4 cm^{-1}) at different temperatures. The sample was dosed with two successive pulses of pyridine (10 μl each). Spectrum was recorded at room temperature after an equilibration time of 30 min. The temperature-programmed desorption of pyridine was studied at 298, 373, 473, 573 and 673 K after equilibration for 30 min after attaining the temperature. The spectrum of the neat sample was subtracted from the pyridine adsorbed sample.

2.2.4. FT-IR

The FT-IR spectra were recorded in transmittance mode with a Thermo-Nicolet Nexus 870 FT-IR spectrometer. The spectrometer was equipped with an XT-KBr beam splitter and MCT/A detector. The sample was diluted with KBr (1:100, w/w) and the spectra recorded at room temperature in ambient air using 100 scans with a resolution of 4 cm^{-1}.

2.2.5. In situ diffuse reflectance FT-IR studies (DRIFTS)

The diffuse reflectance FT-IR measurements were carried out under a flow of He in the instrument described in Section 2.2.3. About (30 mg) of finely crushed sample was placed in a sample holder and pretreated at 698 K for 2 h in He flow to remove

adsorbed moisture. The spectrum of neat catalyst was recorded (400 scans with resolution $4\,cm^{-1}$) at 623 K prior to the experiment under He flow. The reported spectra are difference spectra of adsorbed species and neat catalyst.

2.3. Catalytic activity tests

The SCR of NO by propene was carried out at atmospheric pressure in quartz tubular down flow reactor (inner diameter 4 mm). Catalyst powder (750 mg, particle size $< 180\,\mu m$) was placed in the reactor and a thermocouple was inserted in the center of the catalyst bed to measure the temperature. Prior to the reaction the catalyst was activated at 773 K for 3 h in He flow. The typical reactant gas mixture consisting of NO (1000 ppm), C_3H_6 (2000 ppm) CO_2 (10%) and O_2 (5%), 0 or 5% H_2O, 0 or 20 ppm SO_2 gas and balance He were fed from independent mass flow controllers. The online analysis of the effluent gases was carried out by monitoring the relative masses $m/z = 30$ (NO), 28 (N_2), 44 (N_2O, CO_2), 41 (C_3H_6) and 46 (NO_2) as function of time using a mass spectrometer, a chemiluminescence NO_x analyzer and a micro GC (Varian CP 4900) equipped with a molecular sieve 5 Å and a Porapack Q column. The total flow of the inlet gas was set at $250\,mL\,min^{-1}$ to obtain a gas hourly space velocity (GHSV) of $20,000\,h^{-1}$ ($W/F = 0.05\,g\,h\,L^{-1}$). In these studies NO_x and C_3H_6 conversion were calculated as follows:

$$NO\ conversion\ (\%) = \frac{[NO_x]_{inlet} - [NO_x]_{outlet}}{[NO_x]_{inlet}} \times 100$$

$$C_3H_6\ conversion\ (\%) = \frac{[C_3H_6]_{inlet} - [C_3H_6]_{outlet}}{[C_3H_6]_{inlet}} \times 100$$

3. Results and discussion

3.1. Structural and textural properties

Table 1 shows the BET surface area of all the samples prepared in this study and changes after 20 ppm SO_2 exposure under dry atmosphere. For comparison, the surface area of γ-Al_2O_3 is also included. Upon introduction of Ag in the γ-Al_2O_3 support and the addition of 1 wt% SiO_2 or TiO_2 to AgAl catalyst, the surface area decreased. This is due to the blocking of the pores of γ-Al_2O_3 after impregnation of the support with other metal oxides resulting in the decrease in surface area. Subsequent decrease in specific surface area is also noticeable for used catalysts. Similar tendencies were earlier reported and ascribed to blockage of the pores by the accumulated sulphur [19]. Fig. 1 shows the XRD pattern of the fresh sample (Fig. 1A) and those recorded after exposure to the gas stream containing 20 ppm SO_2 at 623 K (Fig. 1B). The diffraction pattern of fresh AgAl, AgSiAl and AgTiAl (Fig. 1A) show characteristic X-ray lines of γ-Al_2O_3 located at $2\theta = 36.7°$, $46.0°$, $60.70°$ and $66.90°$ (JCPDS: 29-0063). No peak due to bulk metallic Ag or Ag_2O species were observed indicating that the Ag is well dispersed over the support and is amorphous due to low silver loading (2 wt% Ag). Additionally, no peak corresponding to SiO_2 phase or TiO_2 was seen in AgSiAl and AgTiAl respectively. This showed that the structural property of γ-Al_2O_3 support was maintained even after incorporation of SiO_2 or TiO_2. Fig. 1B shows the XRD patterns of the used catalysts exposed to 20 ppm SO_2 in the reaction feed at 623 K. All the samples exhibit the characteristic peaks of γ-Al_2O_3 and no X-ray line corresponding to bulk Ag_2SO_4 was observed in the diffraction patterns of any of the samples.
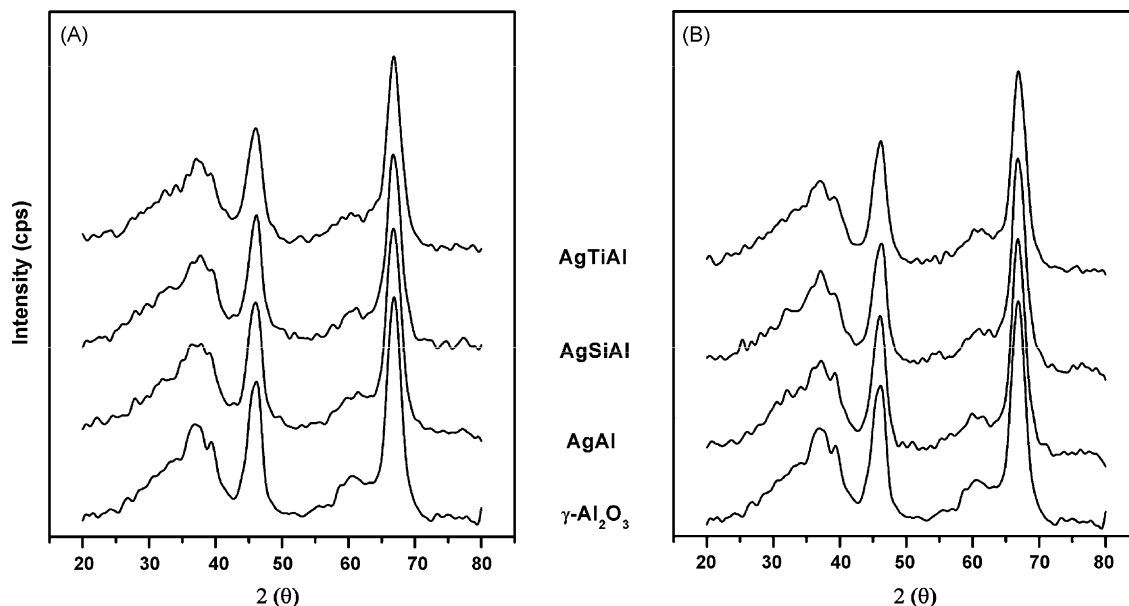
Table 1
Changes in specific surface area of the catalysts before and after SO_2 exposure under dry atmosphere (in the absence of water).

Samples	Surface area (fresh catalysts) ($m^2\,g^{-1}$)	Surface area (after exposure to 20 ppm SO_2)	Relative loss in specific surface area	Sulphur content, wt% (After exposure to 20 ppm SO_2)*
γ-Al_2O_3	237	–	–	–
AgAl	216	198	0.08	0.14
AgSiAl	192	190	0.01	0.05
AgTiAl	190	186	0.02	0.00

* By EDAX analysis.

Fig. 1. (A) X-ray diffraction pattern of fresh γ-Al_2O_3 and the different samples before the reaction and (B) of fresh γ-Al_2O_3 and the samples after the reaction with 20 ppm SO_2 in the feed. Reaction conditions: 1000 ppm NO, 2000 ppm C_3H_6, 10% CO_2, 5%O_2, 0 or 20 ppm SO_2, He balance, temperature 623 K.
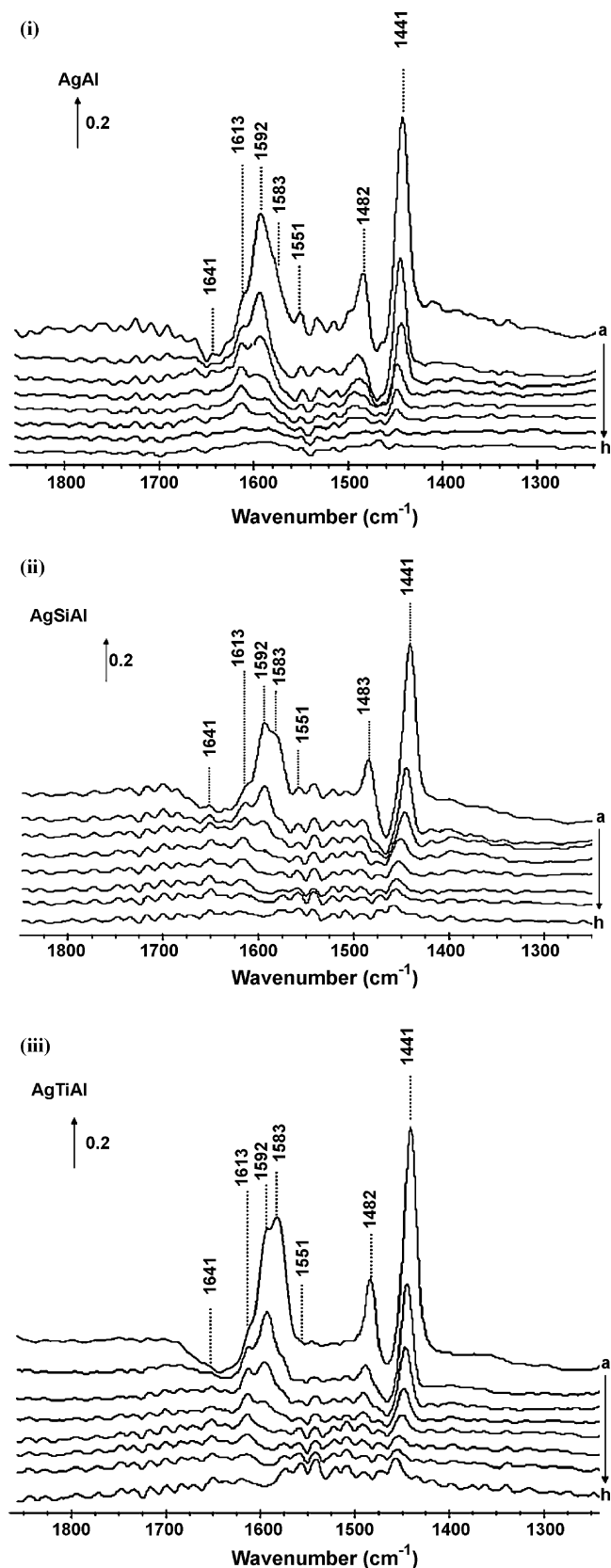
Fig. 2. FT-IR spectra of pyridine adsorbed on the samples followed by evacuation at: (a) 298 K, (b) 373 K, (c) 423 K, (d) 473 K, (e) 523 K, (f) 573 K, (g) 623 K and (h) 673 K.

3.2. Pyridine adsorption study

Nature of acidity was determined by FTIR of adsorbed pyridine and the results are shown in Fig. 2. IR bands appear at 1441, 1482, 1583, 1592 and 1613 cm^{-1} with a weak contribution at 1551 cm^{-1} in spectra recorded at room temperature on AgAl, AgSiAl and AgTiAl. As observed, no significant shift related to changes in charge disturbance in the pyridine ring due to adsorption on stronger acidic sites occurs according to the nature of the additive [20]. Only slight changes are observed in the relative intensity of the bands at 1592 and 1583 cm^{-1}. Previous characterization of Pt/Al_2O_3 by pyridine adsorption corroborates our observations on AgAl with the existence of six contributions, which essentially characterize pyridine adsorption on Lewis acid sites (LAS) [21]. Previous adsorption studies carried out on silica-alumina catalysts [20–22] showed that pyridine adsorbed on LAS essentially gives characteristic infrared bands at 1450 (ν_{19b}) and 1610 cm^{-1} (ν_{8a}) whereas pyridine adsorbed on Brønsted acid sites (BAS) shows characteristic bands at 1545 (ν_{19b}) and 1630 (ν_{8a}) cm^{-1} Additionally, the IR bands at 1482, 1583 and 1592 cm^{-1} can be assigned to weak adsorption of pyridine via hydrogen bonding. Clearly, no significant increase in the relative intensity of the 1551 cm^{-1} band characteristic of pyridinium ions on Brønsted sites is observed particularly after SiO_2 incorporation. Hence, infrared spectra of all the samples show the predominance of LAS on γ-Al_2O_3.

In all the three samples the IR band at 1592 cm^{-1} completely disappears on heating at 473 K, indicating its attribution to weakly interacting species. From Fig. 2 it can be seen that, the shoulder at 1613 cm^{-1} and the band at 1441 cm^{-1} disappears after heating AgAl at 623 K. In contrast over AgSiAl and AgTiAl the shoulder at 1613 cm^{-1} is clearly visible even after heating at 623 K and the band at 1441 cm^{-1} is seen after heating at 673 K. These features indicate the presence of stronger LAS on AgSiAl and AgTiAl compared to AgAl. These general features are in good agreement with pyridine adsorption studies reported earlier on Ag/Al_2O_3 and Ag/TiO_2–Al_2O_3 [23]. These authors reported the presence of stronger LAS on Ag/TiO_2–Al_2O_3 than on Ag/Al_2O_3.

3.3. Catalytic activity

3.3.1. Influence of addition of SiO_2 and TiO_2 to AgAl on the catalytic activity

The SCR of NO_x using propene over Ag/Al_2O_3 and Si/Ti doped catalysts at various temperatures showed only N_2 formation and a complete oxidation of propene into CO_2. No CO formation was observed under dry conditions. It is worthwhile to mention here that no undesirable side product (NO_2) was formed. The overall steady-state conversions of NO and C_3H_6 at different temperatures are shown in Fig. 3, which account for competitive oxidation of C_3H_6 by NO and O_2 according to the following set of reactions:

$$C_3H_6 + 9\,NO = 3\,CO_2 + 3\,H_2O + \tfrac{9}{2}N_2 \tag{1}$$

$$C_3H_6 + \tfrac{9}{2}O_2 = 3\,CO_2 + 3\,H_2O \tag{2}$$
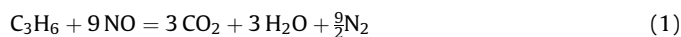
As indicated in Fig. 3, amongst the three catalysts prepared, AgAl showed the highest NO_x conversion (44%) at lower temperature (623 K). At this temperature the NO_x conversion on AgSiAl and AgTiAl was 36 and 38% respectively showing lower overall activities for NO conversion. Similar trend is observed in the case of propene conversion with maximum conversion (20%) on AgAl and least propene conversion on AgTiAl (13% at 623 K). Subsequent comparisons indicate that reaction (2) predominates in the overall temperature range of this study but the relative contribution of the direct oxidation of propene by oxygen on the overall propene
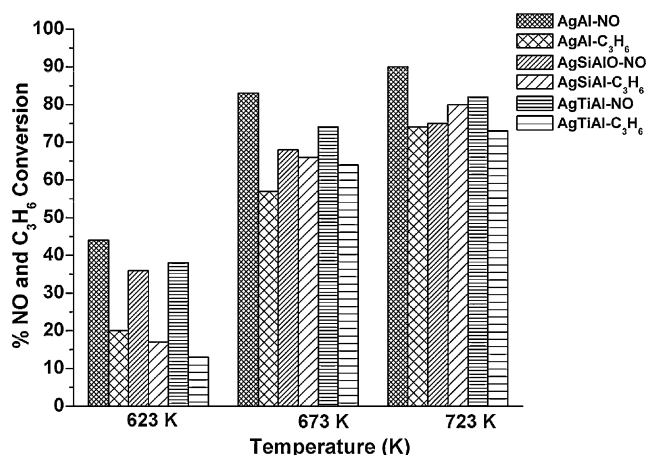
Fig. 3. Conversion of NO_x and C_3H_6 as a function of temperature on AgAl, AgSiAl and AgTiAl in the absence of SO_2. Gas composition: 1000 ppm NO, 2000 ppm C_3H_6, 5%O_2, 10% CO_2, He balance.

Fig. 5. Effect of SO_2 (dry conditions), H_2O and $H_2O + SO_2$ on conversion of NO_x and C_3H_6 on AgAl, AgSiAl and AgTiAl at 623 K. Reaction conditions: 1000 ppm NO, 2000 ppm C_3H_6, 10% CO_2, 5%O_2, 20 ppm SO_2, 5% H_2O and He balance.

conversion accentuates with a rise in temperature. However, it seems obvious that the competition is more in favor of reaction (2) than reaction (1) on AgAl than on AgSiAl and AgTiAl highlighting the promotional effect of Si and Ti on the selectivity behavior. The influence of the amount of additive on the catalytic performances has been examined. AgAl catalysts with 2 wt% SiO_2 (Ag2SiAl) and TiO_2 (Ag2TiAl) were prepared and tested for the SCR of NO_x (Fig. 4). Addition of 2 wt% SiO_2 and TiO_2 resulted in lower NO conversion as compared to AgAl. When conversion of NO at the same temperature (623 K) was compared the following trend was observed: AgAl (44%) > AgSiAl (36%) ~ AgTiAl (38%) > Ag2SiAl (19%) ~ Ag2TiAl (23%). Such a comparison highlights a detrimental effect of increasing amount of SiO_2 and TiO_2 on the overall conversion of NO. On the other hand a selectivity enhancement with a greater ability of the catalyst to activate the C_3H_6/NO reaction at the expense of the C_3H_6/O_2 reaction is evident. Such observations could be tentatively explained on the basis of previous investigations which mentioned the involvement of ad-NO_x species on alumina [8,24] and the participation of Lewis acid sites for the production of oxygenates, both species being considered as intermediate in the DeNO$_x$ reactions [23]. Hence, the above-mentioned experimental observations probably suggest that an optimal amount of Si and Ti additives would determine the
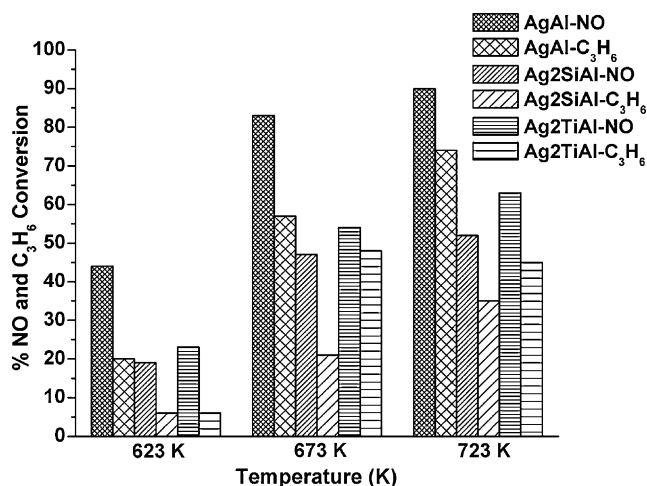
overall performances of Si- and Ti-modified catalysts in the C_3H_6/NO reaction with a detrimental effect at high Ti and Si coverage due to a loss of accessible alumina active sites at the surface partially compensated by an improvement of the acidic properties after Si and Ti incorporation.

3.3.2. Influence of addition of SO_2 on the catalytic activity

All the catalysts in the first series were tested in presence of 20 ppm SO_2 in the absence of water. Fig. 5 shows the effect of SO_2, H_2O and $H_2O + SO_2$ on the catalytic activity at 623 K. It is clearly seen that SO_2 strongly inhibits the NO conversion on AgAl (in the absence of water), decreasing from 44% to 21%. On the other hand, SO_2 does not decrease the conversion of NO significantly on AgSiAl and AgTiAl (Fig. 3). This result underlines the fact that incorporation of Si and Ti has increased the sulphur tolerance of AgAl system. Such an improvement could be partly related to changes in the competitive adsorption of NO_x and SO_x by modifying the acidic properties.

In addition, it is noticed that the deactivation in case of AgAl is also reflected in the loss in the specific surface area (see Table 1) of used catalysts due to sulphur accumulation. This sulphur accumulation on Ag/Al_2O_3 was also confirmed by chemical analysis of sulphur content of the used catalysts using EDAX technique (Table 1). In case of AgSiAl and AgTiAl catalysts no sulphur accumulation was observed in chemical analysis. Previous investigations on the effect of SO_2 on catalyst performances for SCR sometimes lead to controversial observations with reversible or irreversible deactivation and also beneficial effects depending on the catalyst compositions and the nature of hydrocarbons. Angelidis et al. [13] has reported that when 5 wt% Ag/Al_2O_3 is used as catalyst no deactivation due to SO_2 is observed when propene is used as reducing agent as against propane which shows total deactivation in presence of SO_2. Similar tendencies were also reported on Ga_2O_3–Al_2O_3 depending on the method of catalyst preparation [19]. Surprisingly the sol–gel method developed for such a preparation leads to a beneficial effect of SO_2 while co-precipitation and impregnation led to detrimental effects. In fact, Haneda et al. [19] discussed their results in terms of stabilization of sulphate species inducing a negative effect and the creation of Brønsted acid sites, which could activate the conversion of C_3H_6. In case of NSR catalyst also Imagawa et al. [25] have shown that doping of TiO_2 to nanocomposite of Al_2O_3 and ZrO_2–TiO_2 as support has improved the sulphur tolerance of the catalyst considerably which is attributed to the formation of the Al_2O_3–TiO_2 solid solution after addition of TiO_2 to the nanocomposite

Fig. 4. Effect of amount of additive on the conversion of NO_x and C_3H_6 as a function of temperature. Gas composition: 1000 ppm NO, 2000 ppm C_3H_6, 5%O_2, 10% CO_2, He balance.
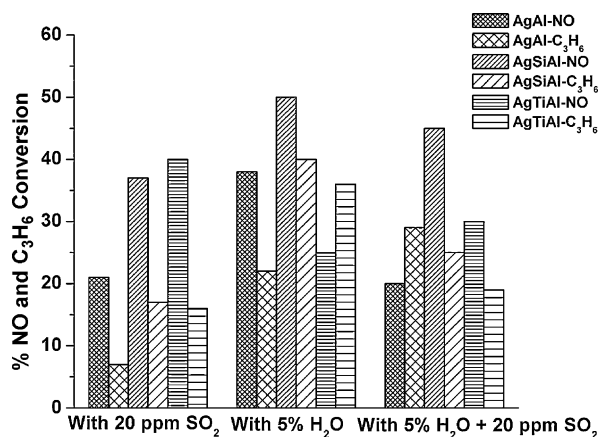
[25]. Our results obtained on AgAl and AgSiAl and AgTiAl could be discussed in the light of those previous statements. As a matter of fact, changes in the selectivity observed on modified-AgAl with a preferential inhibiting effect can be correlated to lower extent of deactivation due to sulphate accumulation which emphasizes the fact that the oxidation of SO_2 to SO_3 is a pre-requisite step for sulphate formation [26]. Further spectroscopic investigations were performed in order to investigate changes in surface properties due to accumulation of S- and N-containing adsorbed species.

3.3.3. Influence of water addition

The influence of H_2O and simultaneous addition of $H_2O + SO_2$ in the feed on the NO conversion to N_2 over the three samples is illustrated in Fig. 5. For these tests, prior to the introduction of H_2O in the feed, the inlet composition was checked at 423 K. The catalyst was then heated to 623 K at 10 K min^{-1} in a water containing flow (5%). After stabilization, the conversion was recorded and then SO_2 was introduced in the feed gas. The activity of the catalyst in the presence of $H_2O + SO_2$ was monitored for 12 h and then the conversion was recorded.

In the presence of water in the feed, AgAl gave a maximum of 38% NO conversion; AgSiAl gave 50% NO conversion whereas AgTiAl gave 25% NO conversion to nitrogen. The corresponding conversions of propene are reported in Fig. 5. Contrarily to previous measurements in the absence of water, CO is significantly formed irrespective of the catalyst composition. The CO formation in presence of water in case of AgAl, AlSiAl and AgTiAl was found to be 134, 425 and 265 ppm respectively confirmed by online GC. Conversion and specific rates for NO reduction to nitrogen have been tentatively estimated for further comparisons. Calculations reported in Table 2 show a decrease in activity in the presence of water except on AgSiAl. In this latter case, a significant rate enhancement in NO conversion is observed. The simultaneous introduction of water and SO_2 induces a significant deactivation except on AgSiAl. As indicated in Table 2, AgTiAl is more sulphur resistant than AgAl, however the most prominent observation is probably the remarkable behavior of AgSiAl with a higher conversion level than that observed in the absence of SO_2 and H_2O. Now regarding the selectivity behavior, SO_2 and H_2O addition induce a weak effect on the selectivity of AgTiAl and AgSiAl. On the other hand, a strong detrimental effect is noticeable on AgAl. Hence, such observations evidence significant changes in catalytic properties after Si and Ti-modification. Earlier investigations on various deNO$_x$ catalysts have discussed a loss of catalytic activity due to H_2O and SO_2 by detailed characterizations of the deactivated

catalyst [27–29]. The loss due to H_2O was attributed to competitive adsorption of H_2O and NO whereas the loss due to SO_2 was attributed to sulphate formation. In the SCR of NO$_x$, when H_2O is present in the feed, it may compete with NO for adsorption on identical reaction sites. The reduction of available adsorption sites for NO by H_2O is one of the main causes for the deactivation of SCR catalyst [27]. Hence, the addition of Si and Ti would weaken the usual inhibiting effect of water. Such an explanation could be still valid for SO_2 which exhibits a weak inhibiting effect. The strengthening of the acidic properties would weaken the interaction between SO_2 and Al_2O_3.

The beneficial effect of water has also been observed for the reduction of NO by heavy hydrocarbons by Shimizu et al. [30]. These authors have tentatively explained their results on the basis of *in situ* IR measurements which suggest a significant reduction of carbonaceous deposits which can cause a poisoning effect. As a matter of fact, He and Yu [31] also reported a promoting effect of water for the C_3H_6–SCR. They observed a rate enhancement in NO and propene conversion but did not find similar effect for the single oxidation of propene by oxygen. However still such an effect is not correctly understood and could possibly involve direct interactions between hydrocarbons and NO$_x$ to explain this beneficial effect. Ag–ZSM5, Ag/SiO$_2$–Al$_2$O$_3$ and Ag/SiO$_2$ are reported to catalyse partial oxidation of methane in presence of oxygen which has been studied using *in situ* FTIR under dry conditions [32]. Ranney et al. have reported beneficial effect of water on propylene partial oxidation using Ag catalyst; Ag(1 1 0) surface [33]. In absence of water complete oxidation of propylene is observed on Ag(1 1 0) where as in presence of water partial oxidation is favored. It is

Table 2
Influence of water and SO_2 on the specific rate of NO conversion to N_2 on modified-Ag catalysts–T(reaction) = 623 K, 1000 ppm NO, 2000 ppm C_3H_6 with $W/F_0 = 0.05$ g h L^{-1}.

Catalyst	Reaction conditions	NO conversion	Specific rate (mol h^{-1} g^{-1})
AgAl	A	0.44	3.6×10^{-4}
	B	0.21	1.7×10^{-4}
	C	0.38	3.1×10^{-4}
	D	0.20	1.6×10^{-4}
AgSiAl	A	0.36	3.0×10^{-4}
	B	0.37	3.0×10^{-4}
	C	0.50	4.1×10^{-4}
	D	0.45	3.7×10^{-4}
AgTiAl	A	0.38	3.1×10^{-4}
	B	0.40	3.1×10^{-4}
	C	0.25	2.1×10^{-4}
	D	0.30	2.5×10^{-4}

A: in the absence of water and SO_2.
B: in the presence of 20 ppm SO_2.
C: in the presence of 5 vol% H_2O.
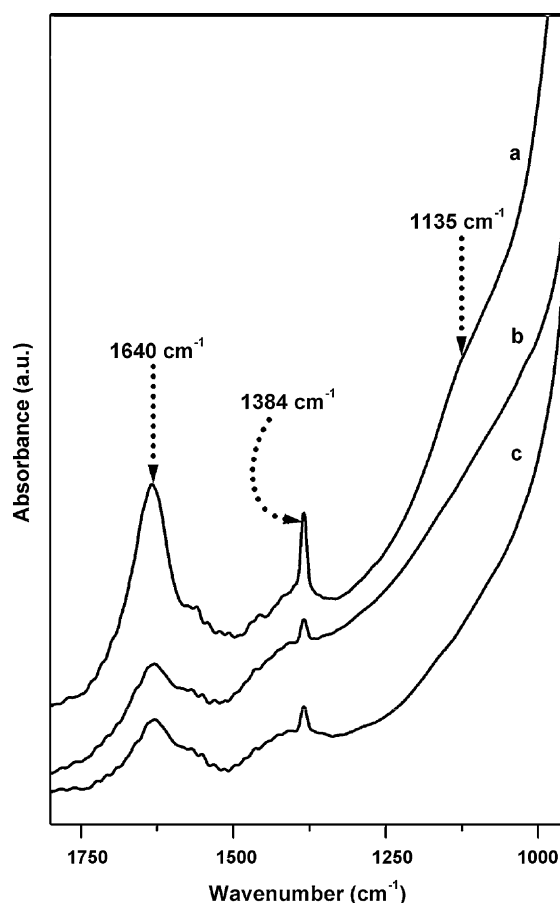D: in the presence of 5 vol% H_2O and 20 ppm SO_2.

Fig. 6. FT-IR spectra of (a) AgAl, (b) AgSiAl and (c) AgTiAl after use in the SCR of NO$_x$ with 20 ppm SO_2. Reaction conditions: 1000 ppm NO, 2000 ppm C_3H_6, 10% CO_2, 5%O_2, 20 ppm SO_2, He balance, temperature 623 K.
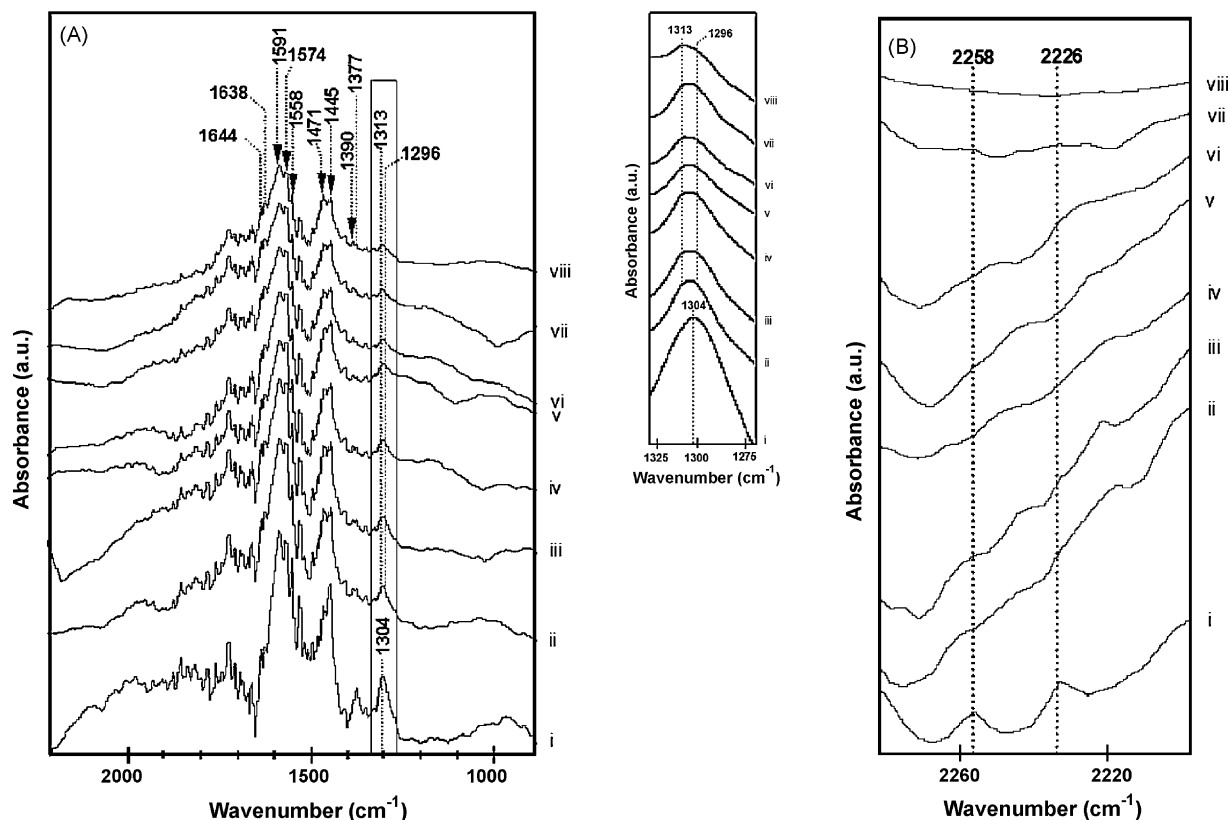
Fig. 7. Dynamic changes of *in situ* DRIFTS spectra over AgAl during the SCR of NO$_x$ in presence of SO$_2$ at 623 K. (i) NO + C$_3$H$_6$–60 min, (ii) NO + C$_3$H$_6$ + SO$_2$–10, (iii) 30, (iv) 60, (v) 120, (vi) 180 min (vii) 240 and (viii) 300 min. Gas composition: 1000 ppm NO, 2000 ppm C$_3$H$_6$, 5%O$_2$, 10% CO$_2$, 20 ppm SO$_2$, He balance.

noticeable that water addition in the feed in our experiments is accompanied with the parallel formation of CO (AgAl 134 ppm, AlSiAl 425 ppm and AgTiAl 265 ppm). In the present case the increase in the propylene conversion as well as NO$_x$ conversion on AgSiAl could be attributed to partial oxidation of propylene to CO, CO$_2$ and hydrogen by comparison with the literature reports. However the exact reaction pathway for the formation of CO and hydrogen in presence of water under the experimental conditions of present study is not very clear. Though CO formation has been detected using online GC analysis, the corresponding hydrogen could not be detected due to reactive nature of hydrogen at reaction temperature (623 K). Satokawa et al. [34,35] have reported positive effect of hydrogen on NO conversion using Ag/Al$_2$O$_3$ catalyst and light hydrocarbons as reductant at lower temperature. Hence the formed hydrogen in presence of water on AgAl, AgSiAl and AgTiAl is expected to react with NO under reaction conditions unabling H$_2$ detection by GC.

3.4. FTIR study of spent catalysts

To study the nature of species formed during SCR in presence of 20 ppm SO$_2$, which are responsible for catalyst poisoning, the FTIR of the used catalyst was examined (Fig. 6). Since the measurements were made in ambient air, the absorption band at 1640 cm^{-1}, due to bending vibration of adsorbed water, was seen over all the samples. The spectrum of AgAl (Fig. 6a) shows an intense band at 1384 cm^{-1} and a broad hump at 1135 cm^{-1} which are assigned to asymmetric and symmetric stretching vibration of O=S=O of sulphate species on Al$_2$O$_3$ [19]. The appearance of these peaks indicates the formation of aluminum sulphate species on the support. In contrast, a much less intense peak at 1384 cm^{-1} is observed in case of used AgSiAl (Fig. 6b) and AgTiAl (Fig. 6c). It is reported that the sulphates formed on Al$_2$O$_3$ are thermally more

stable and decompose at temperature ∼1073–1193 K [15] to yield the oxide whereas those formed on SiO$_2$ [17] or TiO$_2$ [18] are relatively less stable. These results show that sulphate species formed on AgSiAl and AgTiAl get easily desorbed from the surface thus preventing the sulphation of the Al$_2$O$_3$ support and thereby preserving the catalytic activity in presence of SO$_2$.

3.5. In situ DRIFTS study

In order to examine the cause of catalyst deactivation in presence of SO$_2$, and to study the mechanism of deactivation, *in situ* FTIR studies were carried out in the absence of water. Since the deactivation due to SO$_2$ was more prominent at 623 K the *in situ* DRIFTS analysis was carried out at this temperature. Two sets of experiments were carried out for each catalyst. In the first experiment, standard SCR gas mixture (NO: 1000 ppm + C$_3$H$_6$ 2000 ppm + 10% CO$_2$ + 5% O$_2$) was passed over the catalyst at 623 K and the species formed were monitored as a function of time. In second experiment along with standard SCR mixture, 20 ppm SO$_2$ was introduced in the feed at 623 K and the formation of different species was monitored as a function of time. The *in situ* IR results of SCR in presence of 20 ppm SO$_2$ on AgAl, AgSiAl and AgTiAl are shown in Figs. 7–9 respectively. For reference the spectrum in absence of SO$_2$ (exposed to 1000 ppm NO + 2000 ppm C$_3$H$_6$ + 10% CO$_2$ + 5% O$_2$ for 60 min) for AgAl [Fig. 7A (i)], AgSiAl [Fig. 8A(i)] and AgTiAl [Fig. 9A(i)] is also included. Based on previous literature data [24,36,37], IR bands assigned to monodentate nitrate (1250, 1550 cm^{-1}), bidentate nitrate (1305, 1590 cm^{-1}), acetate species (1460, 1585 cm^{-1}), formate species (1595, 1390, 1380 cm^{-1}), enolic (1637 cm^{-1}) and NCO species (Ag-NCO 2235 cm^{-1} and Al-NCO-2259 cm^{-1}) are summarized in Table 3. For all three catalysts in absence of SO$_2$ [Fig. 7A(i)] the characteristic infrared bands due to acetates (1574, 1445 and 1471 cm^{-1}), formates (1390 and
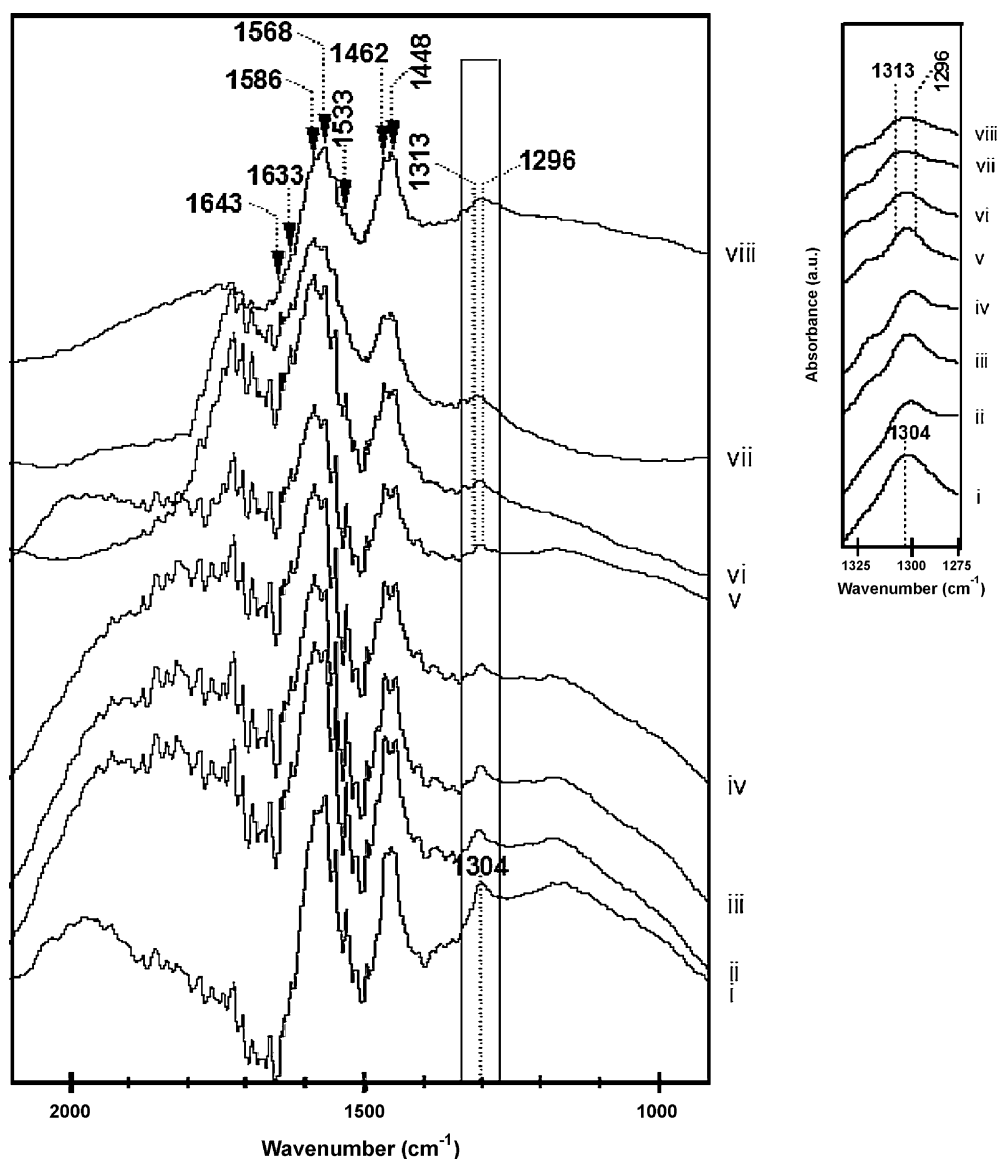
Fig. 8. Dynamic changes of *in situ* DRIFTS spectra over AgSiAl during the SCR of NO$_x$ in presence of SO$_2$ at 623 K. (i) NO + C$_3$H$_6$–60 min, (ii) NO + C$_3$H$_6$ + SO$_2$–10, (iii) 30, (iv) 60, (v) 120, (vi) 180 min (vii) 240 and (viii) 300 min. Gas composition: 1000 ppm NO, 2000 ppm C$_3$H$_6$, 5%O$_2$, 10% CO$_2$, 20 ppm SO$_2$, He balance.

1377 cm^{-1}) and adsorbed nitrates (1638, 1591 and 1304 cm^{-1}) [30] are observed along with surface isocyanate species, Ag-NCO and Al-NCO (2226 and 2258 cm^{-1} for AgAl; 2229 and 2261 cm^{-1} for AgSiAl and 2226 and 2255 cm^{-1} for AgTiAl) [36] as well as surface enolic species (H$_2$C=CH–O–M) (1644 cm^{-1}) [24].

Meunier et al. [36] have studied SCR using propene on Ag/Al$_2$O$_3$ by *in situ* FTIR. Two broad absorption ranges with an apparent maximum at 1560 and 1300 cm^{-1} after exposure to NO + O$_2$ are reported. These observations are in qualitative agreement with that reported in Figs. 7A(i), 8A(i) and 9A(i) and would correspond to the formation of bidentate nitrates species on alumina. A distinct observation is related to the IR band at 1445 cm^{-1} with a shoulder at 1474 cm^{-1} (Fig. 7A) which would result from the direct interaction between propene and NO + O$_2$ with the formation of oxygenates from the partial oxidation of propene. Those IR bands could characterize the presence of carboxylate species according to previous assignments [36]. Weak contributions evident at 1644 and 1377 cm^{-1}, could also highlight the presence of organo-nitrite, oxime and organo-nitro compounds. Weak IR bands are also observed near 2226 cm^{-1} previously assigned to –NCO species. Such tentative assignments seem to agree with those reported by

Li et al. [23] who investigated the reduction of NO by propene on Ag/TiO$_2$–Al$_2$O$_3$ and Ag/Al$_2$O$_3$. These authors suggested the formation of monodentate, bidentate and bridge nitrate, acetate species, formate species and isocyanate species.

The influence of SO$_2$ on the formation of suggested reaction intermediates on the catalyst surface was examined. IR spectra recorded on AgAl in the course of the NO + C$_3$H$_6$ + O$_2$ reactions with 20 ppm SO$_2$ are presented in Fig. 7A(ii–viii). After exposure to 20 ppm SO$_2$ very weak signal for silver sulphate species starts appearing after 30 min at 1313 cm^{-1} which appears as broadening of the 1304 peak. The broadening of the peak at 1304 cm^{-1} becomes more evident from 30 min to 300 min and the peak broadens with maxima shifted to 1313 and 1296 cm^{-1}. It suggests the formation of silver sulphate species on the catalyst surface leading to deactivation due to sulphur poisoning. After exposure to SO$_2$ the previously discussed IR bands ascribed to acetates, formates and nitrates do not disappear. On the other hand the IR bands associated with Ag-NCO at 2226 and Al-NCO at 2258 cm^{-1} gradually decreases in intensity from 10 min to 300 min. In parallel the broad bands at 1558 cm^{-1} and 1445 cm^{-1} intensify which correspond to the development of nitrates species as well as adsorbed C-containing intermediates. This
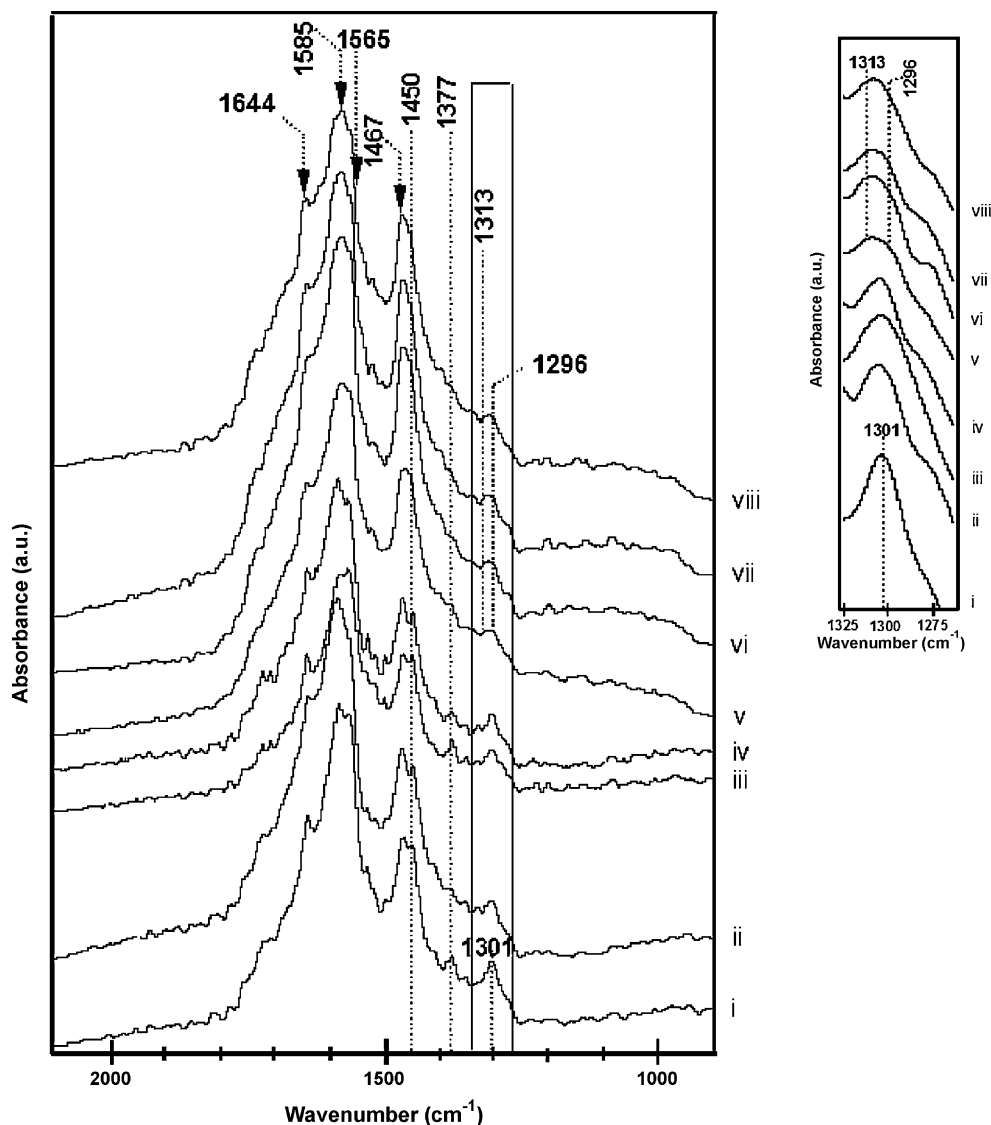
Fig. 9. Dynamic changes of *in situ* DRIFTS spectra over AgTiAl during the SCR of NO$_x$ in presence of SO$_2$ at 623 K. (i) NO + C$_3$H$_6$–60 min, (ii) NO + C$_3$H$_6$ + SO$_2$–10, (iii) 30, (iv) 60, (v) 120, (vi) 180 min (vii) 240 and (viii) 300 min. Gas composition: 1000 ppm NO, 2000 ppm C$_3$H$_6$, 5%O$_2$, 10% CO$_2$, 20 ppm SO$_2$, He balance.

result indicates the sulphation of Ag phase in case of AgAl in presence of 20 ppm SO$_2$.

In case of AgSiAl (Fig. 8) and AgTiAl (Fig. 9) exposure to 20 ppm SO$_2$ shows formation of Ag-sulphate at 1313 cm^{-1} only after

120 min (Figs. 8A(v) and 9A(v) inset). The delayed formation of silver sulphate in case of AgSiAl and AgTiAl proves the improved sulphur tolerance of both the catalysts. It is noticeable that the decrease in intensity of the IR band assigned to Ag-NCO and

Table 3
Assignments of IR bands formed on AgAl, AgSiAl and AgTiAl during *in situ* studies.

Wavenumber (cm^{-1})	Surface species	Vibrations	Observed wavenumber (cm^{-1})	References
1585	Carboxylate COO$^-$	ν^a_{OCO}	1586	[36]
1460		ν^s_{OCO}	1456 and 1471	
1595	Formate HCOO$^-$	ν^a_{OCO}	1591	[36]
1380		ν^s_{OCO}	1377	
1390		δ_{CH}	1390	
1550	Monodentate nitrate NO$_3^-$	$\nu_{N=O}$	1558	[36]
1250		ν^a_{ONO}	Not detected	
1590	Bidentate nitrate NO$_3^-$	ν_{N-O}	1595	[36]
1305		ν^a_{ONO}	1304, 1301	[36]
1560	Ad-NO$_x$		1558	[36]
1313	Ag2SO$_4$		1313	[8]
1384	Al(SO$_4$)$_3$		Not detected	[8]
1637	H$_2$C=CH–O–M		1644	[37]
2230	Ag–NCO		2226, 2229	[24]
2260	Al–NCO		2255, 2258, 2261	[24]

s = symmetric, a = asymmetric and δ = bending.

Al–NCO on AgSiAl and AgTiAl is not significant compared to AgAl which can be correlated to a lesser deactivation on AgSiAl and AgTiAl than on AgAl due to SO_2 poisoning. The sulphation of Al_2O_3 generally evidenced by the presence of a 1384 cm^{-1} IR band (Al-sulphate) is not significantly observed even after 300 min exposure to SO_2, in case of all the catalysts which may be due to low concentration of SO_2 in the feed gas. Nevertheless, it must be mentioned here that the intensities of the IR bands for all adsorbed species in the absence of 20 ppm SO_2 (acetates, nitrates, etc) do not significantly change after SO_2 addition except for AgAl after 300 min SO_2 exposure. This is because the adsorption of NO is known to take place on basic sites and in presence of SO_2 in the feed; there is a site competition between SO_2 and NO_x molecules [38]. Additionally, it is also worthwhile to note that the higher amount of nitrates, acetates on AgAlSi and AgTiAl correspond to a more extensive accumulation of isocyanate species both on Ag and alumina which seems to be well in agreement with previous mechanistic proposals where those adsorbates are supposed to be reactive intermediate for the formation of nitrogen [23].

In this present study, the increased sulphur tolerance of AgSiAl and AgTiAl can be explained on the basis of two factors: acidity of the support and the related extent of interaction between S-containing species and alumina and/or Ag species. The amount of SO_2 deposited onto the support is dependent on the acidity of the support and SO_2 being acidic increase in the acidity of the support results in decrease in the amount of SO_2 adsorbed. The addition of SiO_2 or TiO_2 to AgAl has led to increase in the acidity of the support as mentioned in Section 3.3 [29,39,40]. This increase in acidity has enhanced the SO_2 desorption from the support, thereby reducing the extent of sulphation of the catalytically active phases i.e. Ag and Al_2O_3 and maintaining the high catalytic activity even in presence of SO_2. Secondly, the sulphates of SiO_2 [17] and TiO_2 [18] are known to be thermally less stable than the sulphates of Al_2O_3 [18]. This means that even if the SiO_2 and TiO_2 sites are sulphated, these would desorb more easily from the catalyst support than $Al_2(SO_4)_3$. It is well reported in the literature that role of Ag in Ag/Al_2O_3 system is the partial oxidation of C_3H_6 to form surface enolic species which in turn react with the adsorbed nitrates to form –NCO species, an important intermediate in the SCR of NO_x with C_3H_6 whereas that of Al_2O_3 is to reduce NO_x to N_2 [10]. It may be concluded from the *in situ* DRIFTS results that over AgSiAl and AgTiAl the increase in the catalyst acidity suppressed the sulphur poisoning of Ag and Al_2O_3 sites up to certain extent and the lower stability of the sulphates of SiO_2 and TiO_2 could facilitate the fast desorption of sulphate species from the support thus retaining the activity of the catalysts even in presence of SO_2.

4. Conclusions

The alumina support in case of Ag/Al_2O_3 has been modified for improving sulphur tolerance for SCR of NO_x using propene as reductant. Alumina doping with 1% SiO_2 or 1% TiO_2 has shown a remarkable improvement in the sulphur tolerance. The *in situ* FTIR study has shown that the deactivation of the catalyst is due to the formation of sulphates of Ag and Al_2O_3, which is minimized in presence of SiO_2 or TiO_2. The improved sulphur tolerance is due to the increase in the acidity of the catalyst thus decreasing the

sulphate formation as well as lower stability of the sulphates of SiO_2 and TiO_2.

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